

INTERMETALLIC COATINGS PRODUCED BY MECHANICAL ALLOYING METHOD

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Abstract

The technique of mechanical alloying (MA) was used to coat the metal substrate with other metals. The Al-Ti and Al-Ni binary systems were investigated, at that, all the elements were used both as substrates and as coating powders. Thickness and quality of coating depending on the MA treatment parameters, such as intensity and duration of milling, amount of loaded powder, were investigated. As-synthesized coatings showed structures with high apparent density and free of porosity. However, the surface morphology of the MA-coatings was very rough. Annealing treatment led to the leveling of surface microstructure and formation of different aluminide phases in the coatings. MA allows to produce thick coatings for a relatively short time with good adherence.

Introduction

Aluminides of titanium (TiAl, Ti₃Al, Al₃Ti) and of nickel (NiAl, Ni₂Al₃, NiAl₃) belong to a class of intermetallic heat-resistant materials that are designed for applications at 600-1100 °C. In contrast to conventional structural materials, these alloys have a unique combination of mechanical properties, namely, high specific strength properties and modulus of elasticity that are retained to high temperatures, high high-temperature strength and creep resistance, high resistance to oxidation and combustion; they excel in their characteristics of all modern titanium superalloys. In recent years, thin films of aluminide phases have been an object of great scientific interest [1-5]. First of all, this is connected with the fact that the protective titanium aluminide-based coatings synthesized on the surface of titanium alloys increase by several orders of magnitude the wear resistance and high-temperature oxidation resistance of the matrix while having no considerable influence on its mechanical properties [6-10]. Moreover, the available experimental data show that the chemical reaction at the titanium-aluminum interface can be the basis of new technologies for the fabrication of multilayer and composite titanium aluminide-based materials [11-14]. However, for practical application of new techniques it is necessary to solve a whole series of material-science tasks concerning the stability of evolved structures and kinetics of structural transformations.

Experimental

For the investigation, specimens with dimensions of 8x8x1 mm were prepared from pure titanium and aluminum (99.99%).

Titanium and aluminum powders with a purity of 99.9% and particle size of less than 50 μm were used as starting materials. MA was performed at room temperature in a vibratory ball mill (with amplitude of 12 mm and frequency of 50 Hz) in a steel container with steel balls (Fig. 1). The container and the balls were made of the ShKh 15 steel. The aluminum specimens were charged into the working volume of the mill together with 3.4 g of the titanium powder. The ratio of the ball mass to the powder mass was 10:1. After mechanical alloying, the specimens were annealed under vacuum in a temperature range from 600 to 900 °C and then were cooled in a furnace.

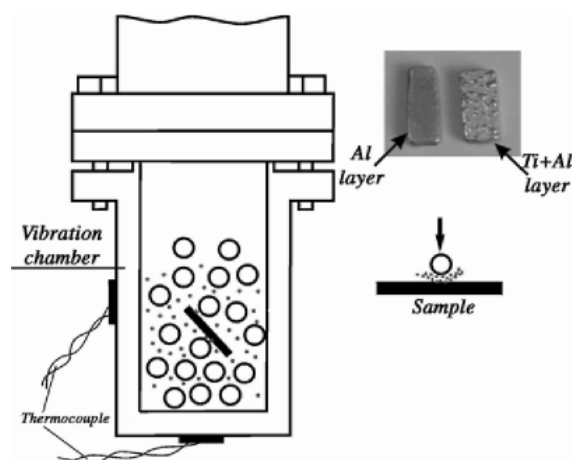


Figure 1. Schematic illustrations of MA method

The phase composition and the crystal structure of the specimens were studied using X-ray diffraction on a DRON-3 diffractometer with CuK_α radiation and scanning electron microscopy in a JCSA-733 microscope.

Results and Discussion

Ti-Al Coatings

Figure 2(a) shows the microstructure of an aluminum specimen with a titanium layer deposited on its surface. The structure synthesized is seen to be lamellar. In the figure, one can see a continuous layer (it is marked with arrows) on which island colonies of particles of different shape and size are formed. The articles are arranged on the surface irregularly; there is no tight contact between them.

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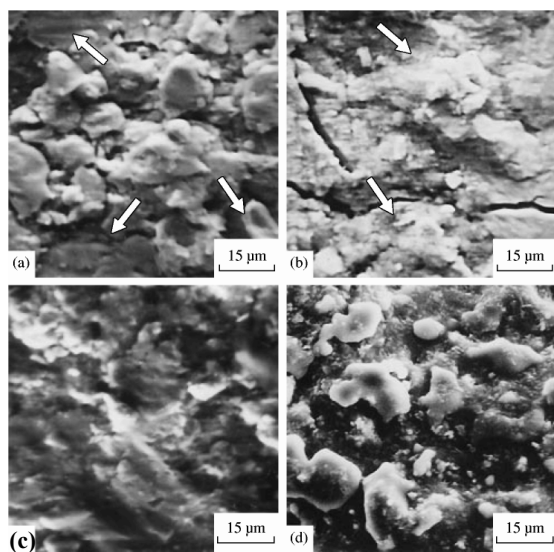


Figure 2. Changes in the microstructure of the titanium layer on aluminum during annealing: (a) the initial specimen; (b) annealing at 600°C for 5 h; (c) annealing at 600°C for 10 h; (d) annealing at 620°C for 20 h

One could presume that at the initial stage of the treatment the titanium particles adhere to the substrates due to their impact interaction and then, at next stages, due to the effect of impinging milling balls, they are deformed and agglomerate. As a consequence, a titanium coating is formed on the aluminum surface, which has a very good adhesion to the surface. Apparently, not only the titanium particles are deformed during the treatment, but also the aluminum surface is affected, which leads to the disturbance of the continuous oxide film on aluminum and the occurrence of regions of direct contact between aluminum and titanium. It is worth noting that it is quite difficult to obtain a similar strength of cohesion by plasma methods.

In case of coating the substrate with Ti+Al mixture we had another kind of surface. The Ti particles were in the Al matrix (Fig. 3(a)). Consequently, it can be assumed that Ti served as a supportive material and Al served as a bonding one. Cold welding between particles and substrate under repeated ball collisions led to the formation of a composite coating. Al flowed into the pores between Ti particles under the impact of balls. As a result a dense Ti+Al coating grew. Cold welding occurred non-uniformly on the sample. Therefore, a very rough surface of Ti+Al coating was formed. In the case of using the powder of pure Al, Al layer with some thickness was coated on the sample but additional cold welding between Al particles and Al layer could not happen. Cold welding might occur in the early stages of MA, when the Al particles were soft, and their tendency to weld was high. Under deformation the particles and Al layer became harder and more brittle. With increase of MA-time, cold welding was restrained. Under the ball collisions, Al coating started flaking and became smoother in comparison with Ti+Al one. In the case of Ti+Al coating, alloying might occur rapidly in the presence of Ti particles. There was no time for the coating to become brittle. It has been found in further investigation that Ti+Al coating could be formed after 30 min trial.

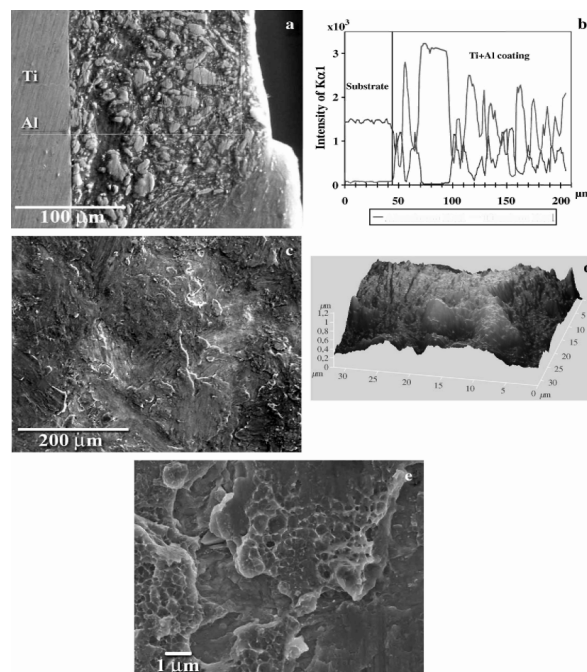


Figure 3. Structure of as-synthesized Ti+Al coating: (a) cross-section; (b) concentration profile; (c) surface microstructure; (d) morphology of Ti + Al coating; (e) dimple structure

Figure 4. shows X-ray diffraction patterns (XRDs) of an aluminum specimen after MA.

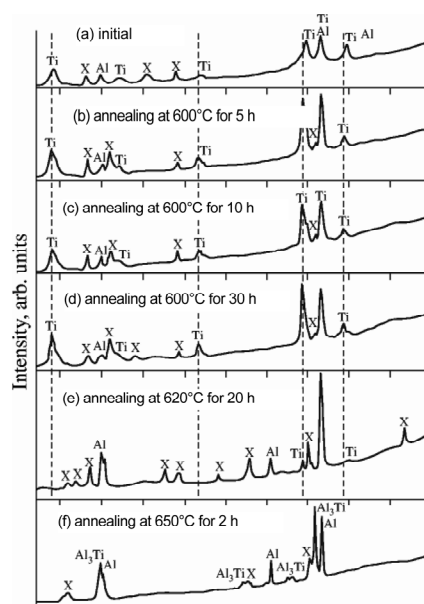


Figure 4. X-ray diffraction patterns of an aluminum specimen with a titanium coating annealed using different annealing temperatures and durations: (a) the initial state; (b) annealing at 600°C for 5 h; (c) annealing at 600°C for 10 h; (d) annealing at 600°C for 30 h; (e) annealing at 620°C for 20 h; and (f) annealing at 650°C for 2 h. X correspond to reflections of arising phases

In the XRDs, titanium and aluminum peaks are recorded (Fig. 4). The peaks are broadened and smeared, which indicates the presence of large microstrains, which arise as a result of numerous impacts by milling balls, and the nanostructured state of both the titanium particles deposited and the aluminum surface. In addition, diffraction reflections marked as X, with a set of interplanar spacings of 1.64, 1.55, and 1.40 Å, are recorded in the XRDs. It is difficult to reliably identify this phase using only three diffraction reflections, since the most intense lines related to this chemical compound are apparently overlapped with the broadened reflections of titanium. These lines might be attributed to the Al_2Ti compound, which has interplanar spacings 1.64, 1.53, and 1.41 Å, or to the Al_5Ti_3 compound (1.636, 1.548 Å) (hereinafter, the interplanar spacings are given in angstroms (Å)). The above X-ray reflections can also be related to oxide phases; however, these phases have very intense lines at low diffraction angles not overlapping with titanium reflections these lines were not observed in the XRDs.

After annealing at 600 °C for 5 h, cracks appeared at the surface of the specimen (Fig. 2(b)). The appearance of cracks indicates the presence of high internal stresses arising during heating, which might be caused by the difference between the thermal-expansion coefficients of the substrate and the titanium layer, by the lattice misfit, and also by changes in the dislocation structure at the contact boundary. Despite the occurrence of cracks, no peeling of the coating was observed. This indicates a good cohesion between the aluminum substrate and the deposited titanium layer. In the micrograph (Fig. 2(b)) one can see the formation of non-uniform relief regions (marked with arrow). It might be assumed that such a relief is formed due to the coagulation of particles that were observed in the island colonies (Fig. 2(a))

After annealing at 600 °C for 5 h the deformation-induced broadening of the diffraction lines of titanium decreases, the reflections in the XRDs become sharp and significantly shifted toward higher angles, which indicates a decrease in the lattice parameters of the phases (Fig. 4(b)). These changes in the XRDs are attributed to a partial relaxation of micro-stresses and coarsening of the microstructure of the phases as well as to a possible start of solid-state transformations at the contact boundary between Al and Ti. The diffraction reflections with interplanar spacings of 1.64 and 1.40 denoted as X, which were observed in the XRDs after MA, were also recorded after annealing, but the "1.55 reflection" was not observed. Moreover, new reflections with interplanar spacings of 2.30 and 1.45 appeared in the XRDs.

When increasing annealing duration at 600 °C to 10 h, "healing" of cracks, leveling-off of relief areas, and a gradual smoothing of the surface layer take place (Fig. 4(c)). The surface becomes morphologically more uniform and continuous than after previous treatments (Fig. 4(a) and 4(b)). In the XRDs, the titanium reflections become asymmetrically broadened on the lower-angle sides and diffuse scattering appears near fundamental reflections (Fig. 4(c)). Such a change in the XRDs indicates the presence of structural inhomogeneities in the surface layer. The diffraction maxima denoted as X after annealing for 5 h become more perfect with an increase in holding duration to 10 h, which might indicate a coarsening of crystallites of this phase (Figs. 4(b) and 4(c)). With a further

increase in the duration of annealing at 600 °C from 10 to 30 h, a gradual and very slow flattening of the surface continues. Reflections of titanium become more symmetric and the lines are shifted toward higher angles; the diffuse scattering near fundamental reflections is retained (Fig. 4(d)). A new smeared reflection with an interplanar spacing of 1.52 appears in the XRDs.

Thus, a structure with a set of interplanar spacings of 2.30, 1.64, 1.52, 1.45, and 1.40 is formed on the aluminum surface as a result of mechanical alloying and subsequent annealing at 600 °C up to 30 h. It is worth noting that the formation of the structure of the surface layer synthesized by mechanical alloying at 600 °C occurs very slowly; this temperature is not high enough to activate processes of intense interaction between the aluminum substrate and the titanium layer. Correspondingly, the Ti-based structure obtained remains sufficiently stable and exhibits a good cohesion with the aluminum substrate in the given temperature-time interval.

After annealing at 620 °C for 20 h the structure of the specimen became very inhomogeneous and large particles of irregular shape are formed at the specimen surface (Fig. 2(d)). The XRDs exhibit diffraction maxima of aluminum, a single weak titanium reflection, and a set of new lines corresponding to interplanar spacings of 3.16, 2.25, 1.92, 1.79, 1.64, 1.60, 1.44, 1.40, 1.37, and 1.36 (Fig. 4(e)). Note that some of these lines are observed in the XRDs immediately after mechanical alloying, whereas some lines only appear with increasing annealing duration. According to the set of interplanar spacings, these reflections might belong to the Al_2Ti compound (2.23, 1.93, 1.66, 1.58, 1.47, 1.40, and 1.38) or to the Al_5Ti_3 compound (3.12, 2.21, 1.78, and 1.63). After annealing at 650 °C for 2 h, the specimen loses its initial form, which indicates the occurrence of an intense reaction between titanium and aluminum. The XRDs exhibit diffraction maxima of aluminum, Al_3Ti reflections, and weak diffuse lines which were earlier observed after annealing at 620 °C (Fig. 4(f)). So, the final structure that is gradually formed during annealing of the diffusion Al-Ti pair is the Al_3Ti compound.

At present, the Al-rich part of the Ti-Al binary phase diagram remains to be studied insufficiently. According to [19], seven stable aluminide phases with a long-range order (superstructures), namely, TiAl , $\text{Ti}_{1-x}\text{Al}_x$, Al_5Ti_3 , Al_2Ti , $\text{Al}_{11}\text{Ti}_5$, Al_3Ti (h), and Al_3Ti (l), and two metastable phases, namely, Al_2Ti (m) and Al_3Ti (m), have been discovered in the concentration range of 50-76 at. % of aluminum. As is known, the diffusion layers arising sequentially on the surface and in deeper zones of metal correspond to single-phase fields of the metal 1-metal 2 phase diagram within the concentration range from zero to the maximum concentration of metal 2 on the surface. During the interaction of metal 1 with metal 2, only thermodynamically possible phases appear, whereas heterogeneous mixtures located in the equilibrium phase diagram between these phases cannot be formed. Consequently, in our case we can assume that during annealing of the Al-Ti diffusion pair obtained by mechanical alloying first the Ti_3Al_5 compound should be formed or a metastable phase on its basis which is stabilized by deformation fields. Then, gradually, as diffusional saturation occurs, an Al_2Ti -based layer is formed, and finally the Al_3Ti compound appears.

Thus, on the basis of experimental results obtained, we can assume the following. As a result of the impact action upon MA on the surface of aluminum specimens, a nonequilibrium layer enriched in titanium starts to be formed; the process of its formation can be fairly complex. On the aluminum surface, as well as in the forming titanium layer, point and dislocation defects appear which favor the inter-diffusion of the components during further deformation. Such a non-uniform mass transfer can lead to the formation of various atomic configurations. The arising atomic clusters can serve as nucleation sites for any phase that can exist in the Ti-Al system in the equilibrium or nonequilibrium state. During prolonged deformation the development of these nuclei can be determined by both thermodynamic factors and varying cluster compositions. Some nuclei grow while others disintegrate or, changing their composition, form nuclei of new phases; i.e., the final phase composition that is formed on the surface of aluminum specimens during deformation can consist of several intermediate metastable phases that can be stabilized by elastic-stress fields.

During subsequent heating, intermetallide-based phases appear gradually as a result of chemical interactions between titanium and aluminum and then, due to the inter-diffusion, a gradual composition leveling-off and a decrease in the fluctuations of the gradients of the chemical potentials takes place in accordance with thermodynamic principles. The reaction rates are determined by the heating temperature and holding duration. The temperature range of the transformations is 600-650 °C.

Figure 5(a) shows the microstructure of an aluminum layer applied on titanium by MA. The structure of the layer synthesized is continuous and very dense. The traces of impacts of milling balls. Upon impact action of milling balls, the aluminum particles are better compacted on the titanium surface than the titanium particles on the aluminum surface (Fig. 2(a)). The XRDs exhibit broadened diffraction lines of only pure titanium and aluminum (Fig. 4(a)). In the case of deposition of the Ti + Al mixture on the titanium surface, a dense layered structure is formed (Fig. 5(b)). According to the intensity of the aluminum reflections in the XRDs, its volume fraction and, consequently, the thickness of the layer deposited, exceed by several factors these parameters in the layer obtained when a pure aluminum powder was deposited, although the mass of aluminum in the Ti + Al mixture is only half that in pure aluminum. In other words, the addition of titanium favors the deposition of thicker layers of the coating. Apparently, the presence of titanium particles leads to the formation of a thin mixed layered structure of Ti and Al on the titanium surface which has better cohesion with the substrate. Note also that the deformation arising when aluminum or the Ti + Al mixture is deposited on the titanium substrate does not lead to the synthesis of intermetallic phases, unlike the case where titanium is deposited on the aluminum substrate. Presumably, this can be attributed to the fact that the degree of activation achievable during mechanochemical synthesis on the softer aluminum substrates is smaller than that in the case of titanium substrates. After annealing at 600°C for 5 h the Al_3Ti compound is synthesized on the titanium surface covered with an aluminum layer or a Ti + Al mixture. Aluminum is completely spent on the formation of this compound. When heating the specimen with an aluminum layer, the morphological inhomogeneities of the surface layer are gradually leveled-off and its structure become more uniform as compared to the initial state (Fig. 5(c)). In

contrast to the titanium substrate with a deposited aluminum layer, in which case a continuous and very dense structure is formed on the surface during annealing at 600°C, in the case of deposition of a Ti + Al mixture an inhomogeneous finely dispersed structure is formed mainly consisting of equiaxed particles (Fig. 5(d)). Apparently, the formation of such a structure is connected with the fact that the nucleation and growth of Al_3Ti particles take place not only at the substrate-coating interface, but also throughout the whole Ti + Al layer in the places of contact between Ti and Al grains. With increasing annealing duration at 600°C to 15 h, in both cases no considerable changes in the structure of the specimens and their phase composition were observed; hence, the structure obtained remains sufficiently stable in the given temperature-time interval.

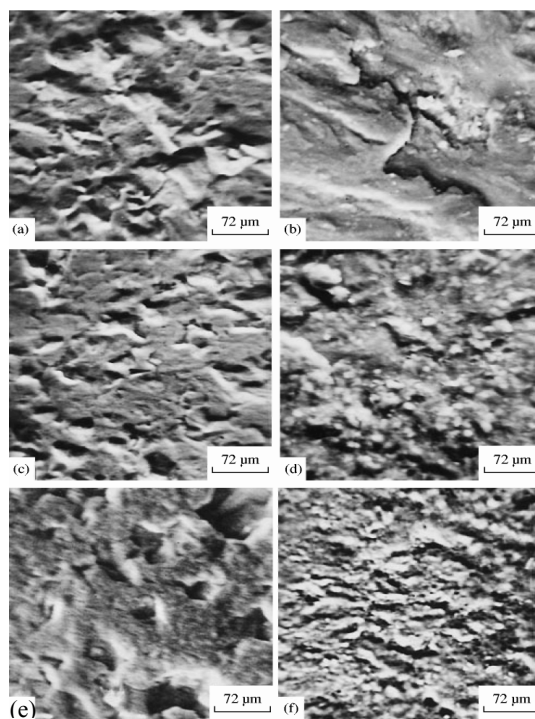


Figure 5. Formation of the structure of aluminide layers on titanium during annealing: (a) the surface of the initial specimen with Al powder deposited by MA; (b) the initial specimen with a Ti + Al mixture deposited by MA; (c) annealing at 600°C for 5 h, Al powder; (d) annealing at 600°C for 5 h, Ti + Al mixture; (e) annealing at 800°C for 2.5 h, Al powder; and (f) annealing at 800°C for 2.5 h, Ti + Al mixture

In the case of a pure aluminum layer on titanium, only Al_3Ti and Ti_3Al compounds were found after annealing on the specimen surface; nevertheless, this does not mean the absence of other possible phases in the series of sequential transformations the regions of existence of the arising phases can be very narrow and the processes of their transformation can proceed very intensely. So, one can assume that the processes of the formation of diffusion layers take place in accordance with the equilibrium phase diagram of Ti-Al. The method of the preparation of diffusion pairs has no considerable effect on the sequence of the transformation processes; however, it shifts the temperature-time intervals of existence of the phases

Ni-Al Coatings

The main features of coating formation described for the Al-Ti system were observed also for the Al-Ni coatings. Ni and Al alloys of different hardness were taken as substrates. The thickness of the substrates was from 5 to 8 mm. Mixture of powders Al+Ni of equiatomic average composition was taken as a material for coating. Besides the vibration ball mill mechanochemical synthesis of coatings in planetary ball mill was also performed. A view of as-coated in vibration ball mill samples is shown in Fig. 6.



Figure 6. Ni-Al coatings fabricated by using vibration mill

Only Ni and Al were found in the as-prepared in vibration mill coating. Further annealing of the samples results in formation of intermetallic phases. XRD analysis showed that at first the phases enriched with Al appear by annealing NiAl_3 and Ni_2Al_3 . Increase of the annealing temperature results in formation of Ni-rich phases, like NiAl and Ni_3Al . The size of crystallites was around 35 nm.

In case of using planetary ball mill, the intermetallic phases started to form just during the MA process under the ball collisions. In that case the size of crystallites of forming intermetallic phases was around 15 nm.

The surface of the samples was studied using SEM. Fig. 7 shows the appearance of the Al substrate coated with Ni-Al that fabricated in planetary mill. The coatings fabricated in the vibration mill were smoother than that fabricated in the planetary mill. For synthesis of intermetallic compound on a surface of the basis metal after formation coating on vibration ball mill heat treatment is required.

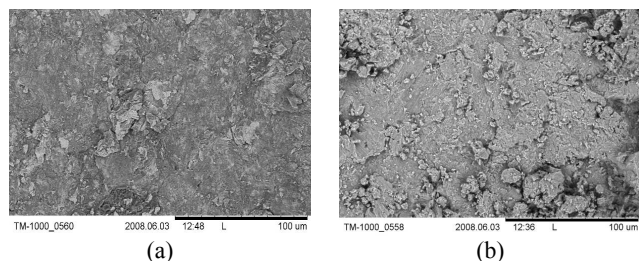


Figure 7. Morphology of the coatings fabricated in vibration mill (a) and planetary mill (b)

The photographs of the Al samples with Al-Ni intermetallic coatings after different treatments are given in Fig. 8. After annealing at 800 °C the coating remained stable in spite of melting of the substrate (Fig.8 (c)).

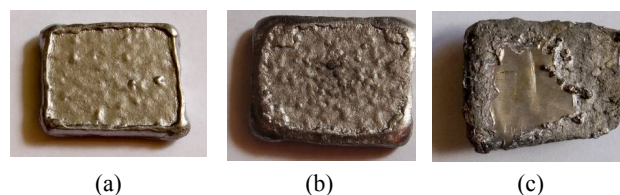


Figure 8. Appearance of the Al substrate coated with Ni-Al fabricated in planetary mill: (a) as-coated, (b) + annealed at 600 °C, (c) + annealed at 800 °C

In general, increase of intensity of MA processing did not influence on the qualitative composition of the coating, however quantitative ratios of amounts of phases changed. Only the most intensive regime of MA during 2 hours results in formation of one more phase - Ni_2Al_3 , which appears due to increase of rate of components diffusion at higher average temperature of process. Annealing of the samples resulted in formation of intermetallic phases in the coatings in accordance with average chemical composition of initial mixture of coated powders; the coating was mainly consisted of Ni_2Al_3 .

As a rule, the thickness of MA coatings increased with time of processing. Figure 9 shows the cross-sectional structure of the coatings. The coating fabricated in planetary ball mill was more homogeneous and showed higher apparent density and adhesion. Besides that the maximal achieved thickness of coatings is higher in case of planetary mill (420 µm) than in vibration mill (250 µm).

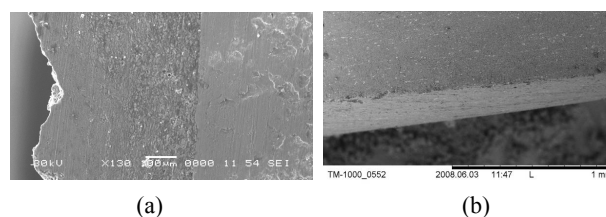


Figure 9. Cross-sectional structure of the coatings fabricated in vibration mill (a) and planetary mill (b)

The conclusion that follows from these experimental results is that the vibration technique may provide a simple and effective procedure for the coating fabrication. The intermetallic compounds may be formed directly under the ball collisions when energy involved in the milling process is increased.

Concluding Remarks

The method of mechanical alloying and subsequent annealing has been used to synthesize Ti-Al and Ni-Al coatings. Owing to the impact action of milling balls, powders particles are deposited on the substrates. As a result, corresponding layers with a very good adhesion are formed on the specimen surface. During subsequent annealing, diffusion titanium aluminide-based layers are gradually formed due to the chemical interaction between titanium and aluminum on the specimen surfaces.

The work performed in this field shows the potential of MA for synthesizing intermetallic coatings. This method has the following advantages:

- unlike the case of ion-plasma methods, no special laborious preparation of the specimen surface is required;
- it gives the possibility of producing sufficiently thick layers;
- the layers synthesized have good cohesion with the substrate;
- the composition of the applied mixture can be varied in wide limits, thereby providing the possibility of obtaining multicomponent layers of a desired composition;
- this method is economical.

The disadvantages of this method are the structural inhomogeneity of the synthesized layer, which, however, can be eliminated by subsequent annealing, and the strong distortion of the surface during ball milling. Apparently, the application range of this variant of MA is limited by the size and geometrical characteristics of the surfaces for which it can be used. These disadvantages are not a determining factor and can be overcome when designing a specific coating process.

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